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Evaluation of the SMPS–APS system as a continuous monitor for measuring $PM_{2.5}$, PM_{10} and coarse ($PM_{2.5-10}$) concentrations

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Abstract

Respirable particulate matter (PM) has been linked to mortality and morbidity by a variety of epidemiological studies. This research has led to the creation of a new PM standard for particles with diameters $<2.5\,\mu m$ ($PM_{2.5}$). Since the conclusion of these studies, many leaps have been made in the realm of continuous particle measurement. Because the literature is still dominated by 24-hour averaged data, the US Environmental Protection Agency still uses this time average as the basis of its federal reference method, despite the fact that PM varies on much shorter time intervals. The purpose of this work is to compare the Scanning Mobility Particle Sizer and Aerodynamic Particle Sizer tandem (SMPS–APS) to other continuous PM measurement devices and to time-integrated mass samplers. The instruments used for comparison include the DataRAM nephelometer, Micro-Orifice Uniform Deposit Impactor (MOUDI), and Partisol Dichotomous Sampler. The data was collected over 4–5 months at various sites in the Los Angeles basin. The results show excellent agreement between the SMPS–APS and the mass based MOUDI and Partisol samplers for $PM_{2.5}$. The DataRAM and SMPS–APS continuous monitors show robust correlation with each other when relative humidity $<70\%$. The coarse fraction ($PM_{2.5-10}$) measured by the Partisol, however, does not track well with the same size range measured by the APS. Several sources of sampling error are discussed to account for this. Finally, mass concentrations collected in individual size ranges of the MOUDI were compared with those determined by the SMPS. While the size ranges from 0.32 to $10\,\mu m$ agree between samplers, the size ranges $<0.32\,\mu m$ are significantly different from MOUDI to SMPS, probably due to the differences between the aerosol sizing principles underlying each technique.
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1. Introduction

Population exposures to ambient particulate matter (PM) have recently received considerable attention as the result of findings from epidemiological studies, which showed associations between ambient particulate concentrations and mortality (Dockery et al., 1996, 1993; Schwartz and Dockery, 1992). Most if not all of the abundant literature of epidemiological studies has been based on particle concentrations averaged over 24 hours or more, primarily due to the lack of adequate samplers that could provide continuous or semi-continuous (i.e., every 1–2 h) information on the particle mass concentration. Largely based on these studies, the

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US Environmental Protection Agency (US EPA) has promulgated a new National Ambient Air Quality Standard (NAAQS; Federal Register, 1997) for fine PM ($PM_{2.5}$; PM $<2.5\,\mu m$ in aerodynamic diameter). This new standard is in addition to the preexisting standard for PM_{10} (including particles having aerodynamic diameters from 2.5 to 10 μm). For both standards, the federal reference method (FRM) is based on the gravimetric analysis of particle filters collected over a period of 24 hours. Nevertheless, the values of key atmospheric metrics influencing ambient particle concentration and size distribution, such as the emission strengths of particle sources, temperature, relative humidity (RH), wind direction and speed and mixing height fluctuate in time scales that are substantially shorter than 12–24 hours. Individual human activity patterns also vary in time periods considerably shorter than 24 hours. The need for developing monitors that measure particle concentration in shorter time intervals (on the order of 1–2 h, or less) is therefore of paramount importance to environmental health, as it leads to substantial improvements in exposure assessment to ambient particulates. Moreover, attempting to obtain a better time resolution for ambient particle concentrations routinely for large monitoring networks is presently impractical with the traditional time-integrated PM_{10} or $PM_{2.5}$ samplers based on gravimetric determination of particle concentration.

A continuously increasing literature describing the development and evaluation of continuous PM monitors has emerged over the past decade Chueinta and Hopke (2001) evaluated a beta-gauge monitor designed to provide near-continuous (e.g., hourly) aerosol PM_{10} mass measurements. The bias between beta gauge and the FRM gravimetric method was found to be 6% on average when examining particles of different composition. Chang et al. (2001) investigated differences between the 24-hour average PM_{10} concentrations of the Wedding beta-gauge monitor and the PM_{10} FRM (Andersen or Wedding) samplers. When the ambient aerosol was diffusion-dried to RH below its deliquescent point, the ratio of beta-gauge PM_{10} to Andersen PM_{10} and Wedding PM_{10} were 1.08 ± 0.06 and 1.09 ± 0.12, respectively. Babich et al. (2000) developed and evaluated a Continuous Ambient Mass Monitor (CAMM™, Andersen Instruments) for fine particle mass ($PM_{2.5}$). The performance of the CAMM was evaluated in a series of field studies, conducted in seven US cities with presumably different $PM_{2.5}$ chemical composition. The 24 1-h CAMM measurements were averaged and compared to the Harvard Impactor (Turner et al., 2000) 24-hour integrated measurement. Excellent agreement was found between the two samplers. For 211 valid sample days, the correlation between the Harvard Impactor and the CAMM concentrations was $R^2 = 0.90$, and the average CAMM-to-HI concentration ratio was 1.07 (± 0.18). In a recent study by Chung et al. (2001), five different continuous monitors were evaluated through comparisons to measurements made using reference filter-based samplers at Bakersfield, CA in the winter of 1999. Based on instrument performance, the beta attenuation monitor (BAM™ 1020, Met One Instruments) tracked the FRM measurements well with a linear regression slope of 0.95, an intercept of $1.36\,\mu g\,m^{-3}$, and a correlation coefficient of 0.99. In the same study, comparison between the CAMM measurements and the FRM measurements yielded a regression with a slope of 0.74, an intercept of $10.85\,\mu g\,m^{-3}$, and a correlation coefficient of 0.96. The performances of the BAM and the CAMM were not strongly affected by particle composition or meteorological conditions. The study by Chung et al. (2001) concluded that both the BAM and the CAMM appear to be suitable candidates for deployment in a real-time continuous $PM_{2.5}$ monitoring network. This finding is particularly important, considering the challenging meteorological conditions that prevailed during the study period in the winter of 1998 in Bakersfield, CA, because it corroborates the integrity and robustness of these continuous monitors.

A solid and very reliable method for continuous measurements of coarse (2.5–10 μm) particles has been recently published (Misra et al., 2001). The operating principle of the monitor is based on enriching coarse particle concentrations by a factor of about 25 by means of a 2.5 μm cutpoint round nozzle virtual impactor while maintaining fine mass, i.e., mass of $PM_{2.5}$ at ambient concentrations. The aerosol mixture is subsequently drawn through a Tapered Element Oscillating Microbalance (TEOM™ 1400A, Rupprecht and Patashnick, Albany, NY), the response of which is dominated by the contributions of coarse PM due to concentration enrichment.

This paper describes an evaluation of two near-continuous instruments used in tandem to provide $PM_{2.5}$ and PM_{10} concentrations, i.e., the Scanning Mobility Particle Sizer (SMPS™, TSI Model 3936) and the Aerodynamic Particle Sizer (APS™, TSI Model 3320). We refer to the tandem as SMPS–APS. The SMPS–APS system has the advantage over other continuous mass monitors of generating mass concentrations at discrete size intervals near-continuously. This additional feature is important for apportioning sources and better estimating the local deposition and dosimetry of inhalable particles at the full range of particles of interest. The SMPS and APS have originally been designed to characterize aerosols in the laboratory (Smith et al., 1987; Kinney et al., 1991; Page et al., 2000), in occupational environments (e.g., O'Brien et al., 1987; Chen et al., 1998), and more recently, to characterize ambient PM for environmental exposures (e.g., Peters et al., 1997; Abt et al., 2000). The

characterization of the SMPS–APS system described in this study has been conducted continuously over more than a year at several sampling sites of the Los Angeles air basin during separate seasons. Mass concentrations determined for various size fractions (e.g., $PM_{2.5}$ and PM_{10}) by both instruments have compared these measurements to that of filter-based mass measurements, in part to evaluate the utility of the tandem system as a continuous mass monitor for the convenience of obtaining greater time resolution data for health based and source apportionment studies.

2. Methods

2.1. Sampling locations

The SMPS–APS system operated inside a mobile particle laboratory developed by the Southern California Particle Center and Supersite (SCPCS) measurement and monitoring program, funded by the US EPA. During the period of this study, measurements were conducted at 4 sites for about 4–5 months each and across separate seasons. From October 2000 to February 2001, sampling was done in Downey, a typical urban site in south central Los Angeles impacted mostly by primary vehicular emissions. From mid-February to June 2001, sampling was conducted in Riverside, from July to August 2001 in Rubidoux, and from September to December 2001 in Claremont. Riverside, Rubidoux and Claremont are receptor areas of the eastern inland valleys of the basin, in which the aerosol plume generated by the millions of vehicles, mostly west of downtown Los Angeles, is advected by the predominant westerly winds after aging for several hours to a day (Pandis et al., 1992). Rubidoux and Riverside (unlike Claremont) also lie downwind of significant ammonia emissions from nearby farming and livestock, which results in high concentrations of ammonium nitrate (Christoforou et al., 2000).

2.2. Instrumentation

Ambient aerosols were drawn through the SMPS and APS via a common vertical stainless steel tube, 250 cm long and 2.0 cm in diameter, equipped with an elbow-shaped inlet to prevent entrainment of rain droplets. The resulting particle residence time was about 7.5 s, thus small enough to avoid diffusional losses of ultrafine PM. Particle concentration measurements made by the SMPS–APS were compared to measurements with a co-located Microorifice Uniform Deposit Impactor (MOUDI™, MSP Corp. Minneapolis, MN; Marple et al., 1991) and Dichotomous Partisol-Plus™ (Model 2025 Sequential Air Sampler, Rupprecht and Patashnick Co. Inc., Albany, NY; Patashnick et al., 2001). MOUDI and Partisol sampled approximately once per week and for time periods varying from 4 to 24 h, depending on locations and observed pollution levels. Particles were classified by the MOUDI in the following aerodynamic particle diameter ranges: <0.10, 0.10–0.32, 0.32–0.50, 0.5–1.0, and 1.0–2.5 μm. Particles <0.10 μm were collected on an after-filter. We chose to not measure coarse PM with the MOUDI because we were concerned that the high jet velocities of the impactor would result in particle bounce, a phenomenon that would be more pronounced at the larger particle size range (Tsai and Cheng, 1995). The impaction substrate corresponding to the 2.5 μm cutpoint stage of the MOUDI was thus coated with a thin layer of silicone grease (Chemplex™ 710, NFO Technologies, Kansas City, KS) to prevent bounce. Teflon filters with diameters of 4.7 and 3.7 cm (2 μm pore size, Gelman Science, Ann Arbor, MI) were used to collect particles in the remaining MOUDI stages and after-filter, respectively.

The Partisol uses a PM_{10} inlet operating at $16.7\,l\,min^{-1}$ to remove particles larger than 10 μm in aerodynamic diameter. The remaining PM_{10} aerosol is drawn through a virtual impactor, or, "dichotomous splitter", located after the inlet. Two separate flow controllers maintain coarse PM at $1.67\,l\,min^{-1}$ and the fine aerosol stream at $15\,l\,min^{-1}$. Coarse and fine particles are collected on two 4.7 cm Teflon filters, placed in the minor and major flows of the Partisol virtual impactor, which are housed in reusable cassettes. The Teflon filters of both MOUDI™ and Partisol™ samplers were pre- and post-weighed using a Mettler Microbalance (MT5, Mettler-Toledo, Inc, Hightstown, NJ) after 24-hour equilibration under controlled humidity (35–40%) and temperature (22–24°C) to determine particle mass concentrations. The SMPS and APS number-based concentrations were converted to mass concentrations using an algorithm described by Sioutas et al. (1999) and assuming a particle density of $1.6\,g\,cm^{-3}$.

3. Results and discussion

3.1. Fine particle mass ($PM_{2.5}$) concentrations

In Fig. 1, the time-integrated fine particle mass concentrations determined with the semi-continuous SMPS–APS system are compared to those measured gravimetrically by the MOUDI and Partisol filter-based samplers. The data shown in the graph correspond to time periods varying from 4 to 24 h. Geometric mean and standard deviations ratios of the SMPS–APS to either MOUDI or Partisol concentration are summarized in Table 1. Inter-comparisons between all three instruments indicate an overall excellent agreement. The geometric average $PM_{2.5}$ ratios of SMPS–APS to

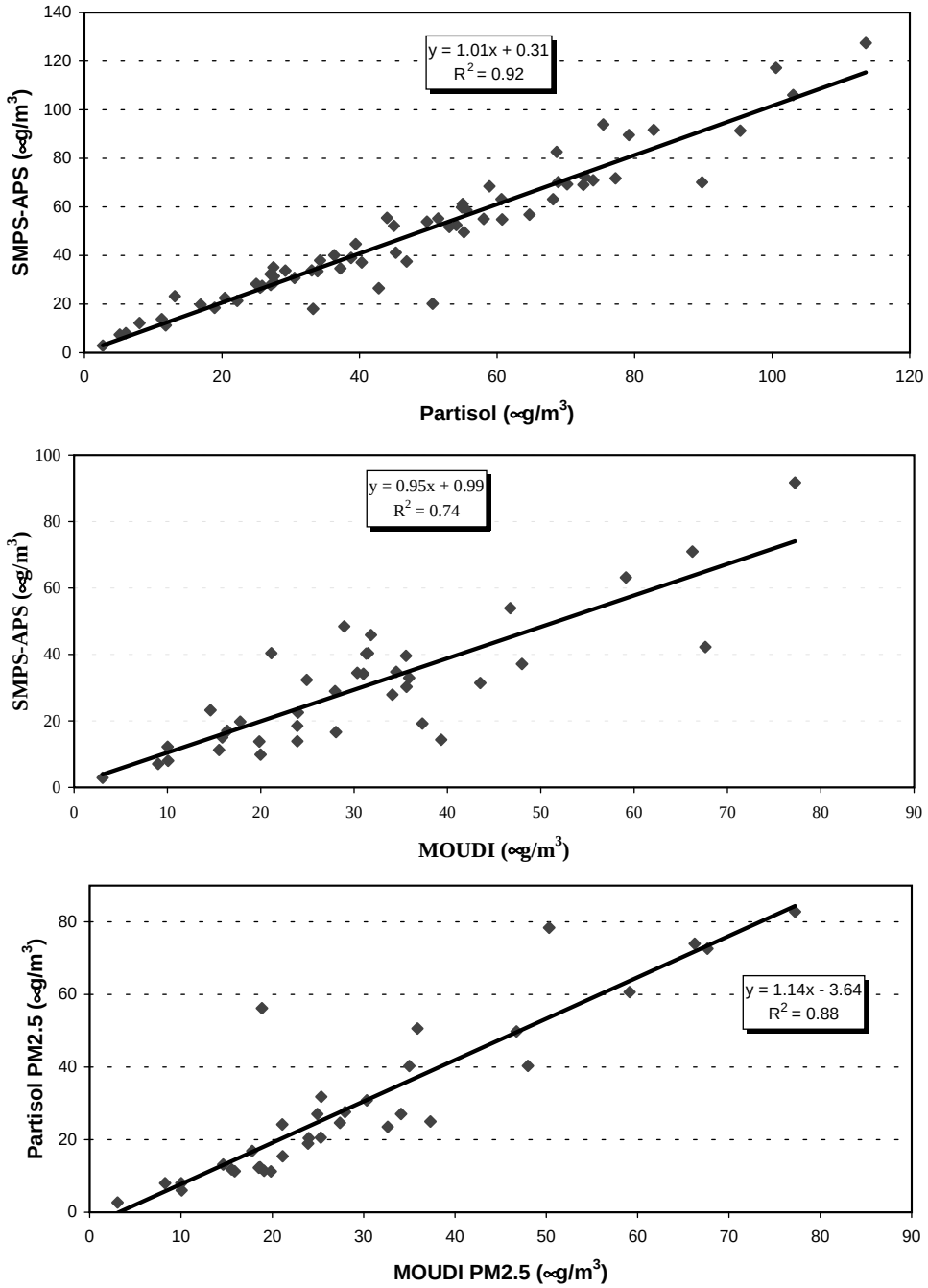

Fig. 1. $PM_{2.5}$ mass concentration comparison between SMPS–APS, Partisol and MOUDI.

Partisol and MOUDI are 1.04 ($\pm$0.11) and 0.97 ($\pm$0.33), respectively. The SMPS–APS concentrations are also highly correlated with both Partisol and MOUDI data: the R^2 for the SMPS–APS vs. the Partisol is 0.92; for the SMPS–APS vs. the MOUDI is 0.74 (The MOUDI-Partisol concentrations are also highly correlated, with $R^2 = 0.88$). Both the results of linear regressions shown in Fig. 1 as well as the data shown in a time-series plot (see Fig. 2) clearly demonstrate that, at the full range of $PM_{2.5}$ measurements, the SMPS–APS consistently agrees with the gravimetrically determined reference mass concentrations of the Partisol and those of the MOUDI impactor.

The only near-continuous monitor to which the SMPS–APS tandem was compared was the DataRAM™ (RAM-1, MIE Inc., Billerica, MA). Comparison between the $PM_{2.5}$ concentrations of these two instruments was conducted only for a 2-month period, from 25 June to 22 August 2001. The DataRAM monitor is an integrated nephelometer and measures continuously the amount of light (with a wavelength, $\lambda = 880\,nm$) scattered by particles drawn through a sensing zone at a flow rate of $2\,l\,min^{-1}$. The amount of light scattered is converted to particle concentration readings. The instrument's performance is based on the well-established light scattering theory. Fig. 3 shows a plot of the hourly $PM_{2.5}$ mass concentrations measured by the SMPS–APS against those measured by the DataRAM. The data plotted in this figure reveal a very high correlation between the $PM_{2.5}$ concentrations measured by the two methods ($R^2 = 0.88$). However, on average, the DataRAM overestimates the SMPS–APS $PM_{2.5}$ mass by a factor of 2.2 (± 0.34). The higher nephelometer readings may be due to the following reasons. First, the concentration readings of any nephelometer increase with RH, primarily due to the increase in the average particle size associated with the condensational growth of hygroscopic PM components as well as additional light scattering by water vapor (McMurry et al., 1996; Sloane, 1984). In our experiments, aerosols were sampled by various monitors after equilibration to the indoor temperature and humidity of the Particle Instrumentation Unit (PIU) trailer. The indoor RH levels varied between 40% and 70%, thus comparable or lower than the deliquescence point of ammonium sulfate and nitrate. A recent study in which DataRAM measurements were compared to gravimetrically measured concentrations (Sioutas et al., 2000) showed that at RH levels as low as 60–70% the DataRAM concentrations are higher than those measured gravimetrically by a factor of about 1.5. Sioutas and colleagues also found that the DataRAMs performance was strongly dependent on the mass median diameter (MMD) of the ambient particle distribution. When the MMD of the distribution is between 0.7 and 1.0 μm, the DataRAM to MOUDI concentration ratio increases to values in the range of 1.4–1.8, a finding that is consistent with the classic Mie theory, in which the maximum scattering is observed in the particle size range that is comparable to the wavelength of the incident light (White et al., 1994). Considering that the wavelength used by the DataRAM is 0.88 μm, maximum scattering should be expected in the 0.7–1.0 μm range. This was further corroborated by the data plotted in Fig. 4,

Table 1
Summary of geometric mean and standard deviations ratios of the SMPS–APS to MOUDI or Partisol concentrations

Instruments compared	Particle size range (μm)	Mean ($\pm$SD)
SMPS–APS to Partisol	$PM_{2.5}$	1.04 ($\pm$0.11)
SMPS–APS to Partisol	PM_{10}	0.96 ($\pm$0.21)
SMPS–APS to Partisol	$PM_{2.5-10}$	0.92 ($\pm$0.64)
SMPS–APS to MOUDI	$PM_{2.5}$	0.93 ($\pm$0.33)
MOUDI to Partisol	$PM_{2.5}$	1.06 ($\pm$0.16)

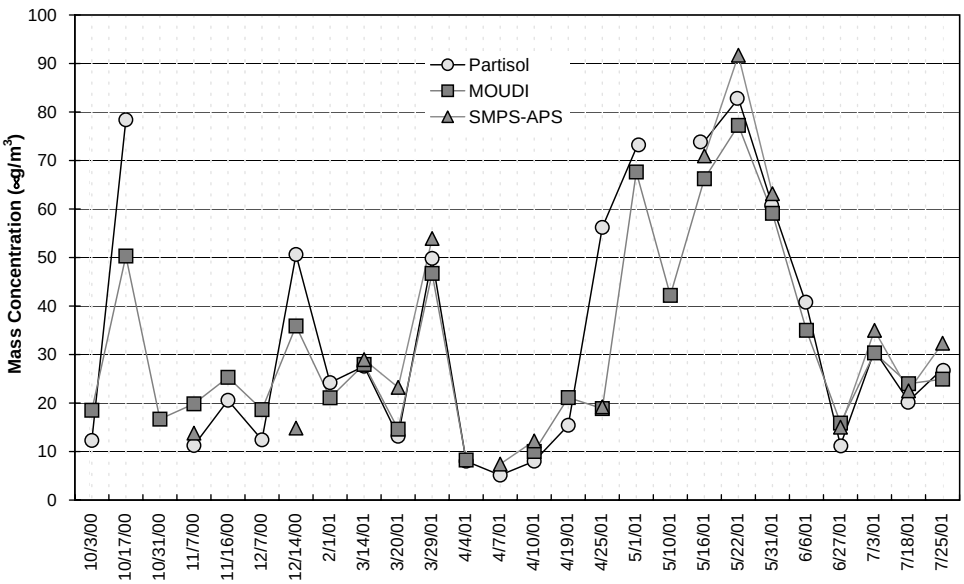

Fig. 2. Daily $PM_{2.5}$ mass concentration comparisons for SMPS–APS, Partisol, and MOUDI.

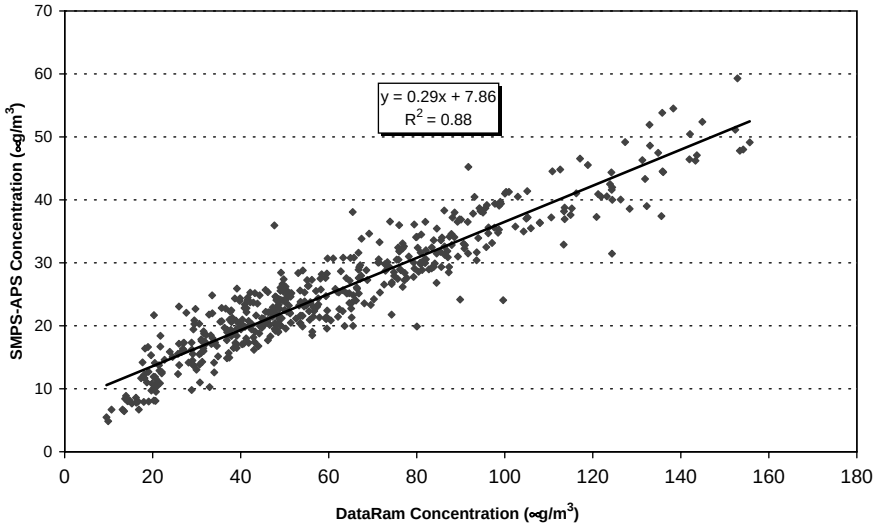

Fig. 3. SMPS–APS concentration vs. DataRAM concentration for $PM_{2.5}$.

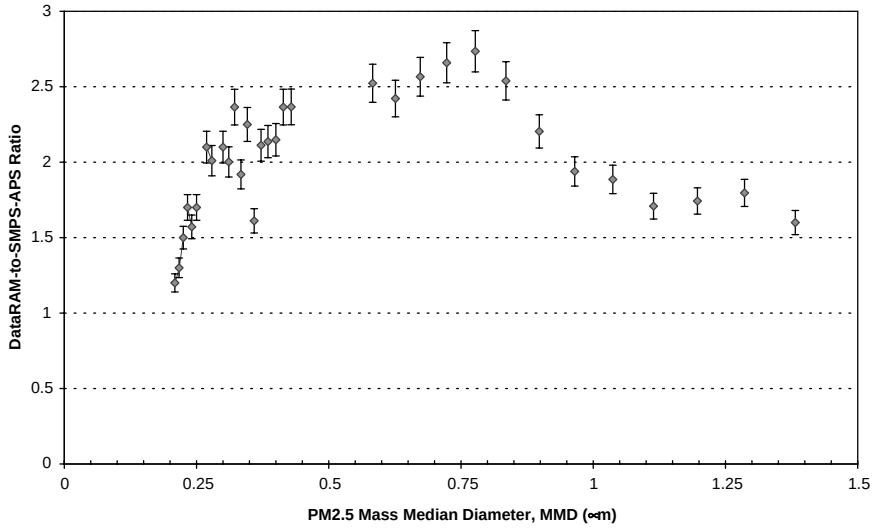

Fig. 4. $PM_{2.5}$ DataRAM to SMPS–APS ratio as a function of the mass median diameter estimated using SMPS–APS measurements.

revealing a similar trend to that observed by Sioutas et al. (2000). Here, the aerosol MMD is based on the calculated mass distribution from SMPS–APS measurements. As evident from the data plotted in Fig. 4, the DataRAM-to-Partisol ratio increases with particle size, reaches a maximum in the 0.7–0.85 μm range, and subsequently decreases with further increase in MMD. In summary, we believe that the overall higher DataRAM readings are attributed to the combined effects of some residual vapor adsorption and mostly of particle size on light scattering.

3.2. PM_{10} concentrations

The SMPS–APS PM_{10} mass concentrations are compared to those of the Partisol in Fig. 5. The agreement between the two instruments is still very good but not as consistent as that observed for the $PM_{2.5}$ concentrations. The geometric average ratio of the SMPS–APS to Partisol concentrations was 0.96 (± 0.21). However, the degree of correlation (R^2) decreases from 0.92 to 0.80. This is primarily due to the influence of the coarse PM ($PM_{2.5-10}$) measurements

of the APS, which will be discussed in the following section.

3.3. Coarse PM ($PM_{2.5-10}$)

Fig. 6 presents a comparison between coarse ($PM_{2.5-10}$) particle mass concentration measured by the APS and the Partisol. A weak correlation was found between the instruments ($R^2 = 0.28$). Although the average ratio of APS to Partisol concentrations was 0.92 (± 0.64), both the relatively large standard deviation of this ratio as well as the weak correlation between the data indicate that there is considerable scatter in the overall agreement between APS and gravimetrically determined concentrations. Further analysis of our data was conducted to investigate whether the APS to gravimetric ratio is dependent on particle size. Coarse PM measured by the APS was divided into 16 size intervals of equal logarithmic length. Results from this analysis are shown in Fig. 7, in which the APS-to-Partisol mass concentrations ratio is plotted against the MMD of the coarse PM mode. This ratio increases as the MMD increases from about 4–5.5 μm and reaches a maximum of about 1.6 for a MMD between 5 and

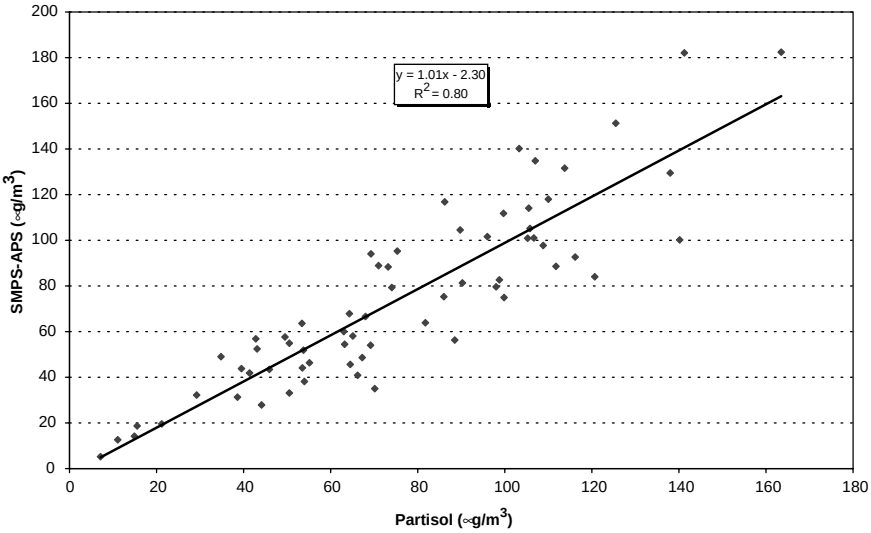

Fig. 5. PM_{10} mass concentration comparison between SMPS–APS and Partisol.

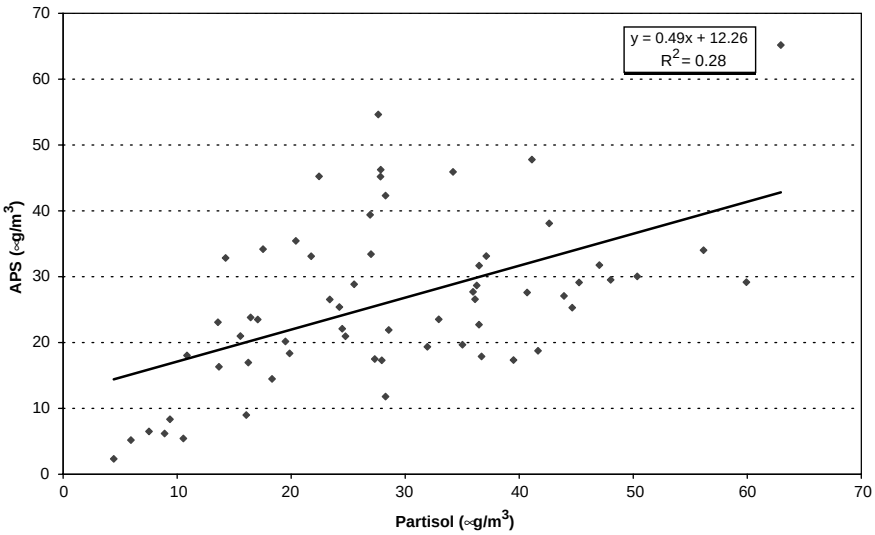

Fig. 6. Partisol vs. APS coarse particle mass concentration comparison.

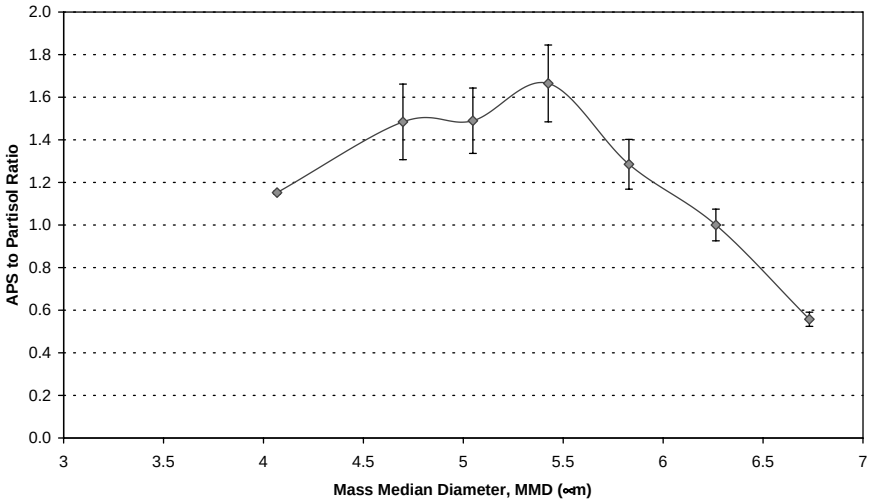

Fig. 7. Partisol to APS ratio for coarse particles ($PM_{2.5-10}$) as a function of mass median diameter.

5.5 μm. The APS to Partisol ratio subsequently decreases sharply to levels below 1 as the MMD exceeds 6 μm.

Several previous studies have compared the size distributions measured by the APS 3320 and those of a cascade impactor. Stein et al. (2000) as well as Armendariz and Leith (2002) showed that for particles larger than approximately 5 μm, artificial particle counts created a distortion of the APS size distribution as compared to that determined gravimetrically by cascade impactors. These so-called "phantom" particles result in overestimations of the true mass concentrations by the APS, a finding that is consistent with our results and explains the somewhat higher concentrations of the APS. The study by Armendariz and Leith (2002) also showed that the counting efficiency of the APS 3320 decreases for particles larger than about 5 μm because of losses of these larger particles inside the APS due to settling and impaction. This explains the decreasing trend shown in Fig. 7 for particles larger than about 6 μm. For that size range, internal APS particle losses apparently are high enough to compensate for the added mass associated with the artificially counted particles. We thus concur with the conclusions and recommendations made by Armendariz and Leith (2002) that the data reported by the APS will need to be adjusted for its counting efficiency in order to yield accurate particle concentrations and size distributions.

3.4. Size distributions measured by SMPS–APS and MOUDI

Fig. 8 shows a size-fractionated comparison between the SMPS–APS and the MOUDI mass concentrations. A summary of the SMPS–APS to MOUDI mass concentrations for a specific size range is shown in Table 2. With the exception of ultrafine particles (i.e., below 0.1 μm) the data appear well-correlated, with R^2 varying from 0.62 to 0.65. Very good overall agreement between the SMPS–APS and MOUDI was obtained for the concentration of particles in the ranges of 0.32–1.0 and 1.0–2.5 μm, with the average SMPS–APS to MOUDI concentration ratio being 0.95 ($\pm$0.24) and 0.94 ($\pm$0.22), respectively. The relative scatter in the data is probably due to variations in the chemical composition of each sub-mode and in each sampling location, which would affect the validity of the assumption, that particle density is 1.6 g cm^{-3} across all size ranges and all sampling sites. The non-aqueous components of ambient fine particles consist primarily of ammonium sulfate (density $\rho_p = 1.8\,g\,cm^{-3}$), ammonium nitrate ($\rho_p = 1.9\,g\,cm^{-3}$), elemental carbon ($\rho_p = 2\,g\,cm^{-3}$) and organic compounds ($\rho_p = 1.0-1.5\,g\,cm^{-3}$). The ratio of organic to elemental carbon in Los Angeles typically ranges from 4 to 7 (Christoforou et al., 2000), thus the density of the composite carbon mixture will be in the range 1.2–1.7 g cm^{-3} and of the dry $PM_{2.5}$ aerosol in the range 1.3–1.9 g cm^{-3}. Local and seasonal variations in the relative amounts of each species per size range might introduce a maximum uncertainty of $\pm$20% to the SMPS–APS mass concentrations based on a density of 1.6 g cm^{-3} (which would explain the scatter of data in the graph), but the overall SMPS–APS to gravimetric ratio is not expected to frequently fall outside the range of 0.8–1.2. As the data plotted in Fig. 8 and summarized in Table 2 indicate, the overall agreement between SMPS–APS and MOUDI is excellent considering the assumptions made. Paired *t*-tests between the SMPS–APS and MOUDI concentrations for the size ranges of 1–2.5

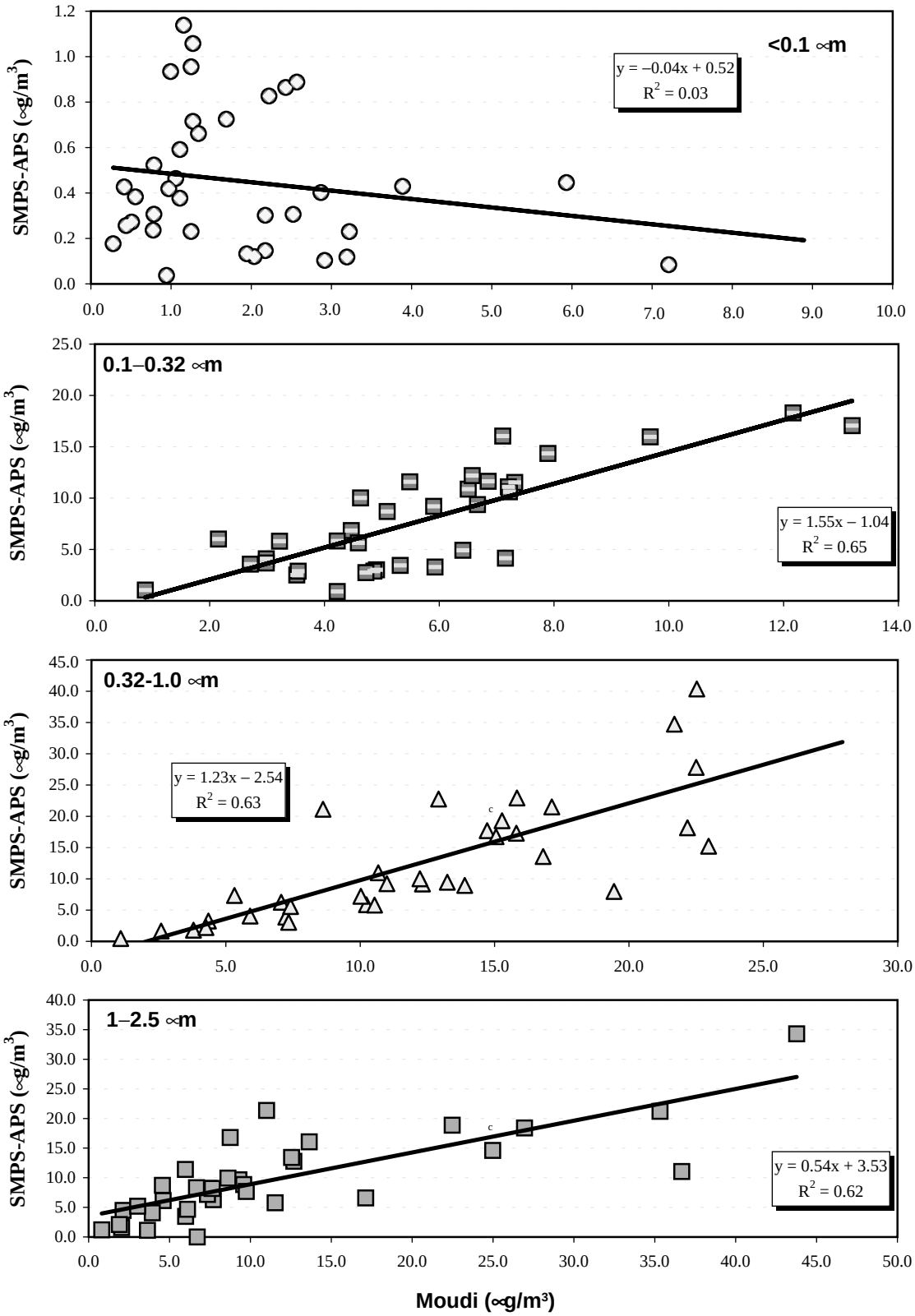

Fig. 8. Size fractionated mass concentration comparison of SMPS–APS and MOUDI.

Table 2
Summary of the SMPS–APS to MOUDI concentration comparisons fractionated by size ranges

Aerodynamic size range (μm)	SMPS–APS to MOUDI concentration mean (±SD)	p-Value[a]
<0.1	0.39 (±0.18)*	<0.001
0.1–0.32	1.37 (±0.35)*	<0.001
0.32–1.0	0.95 (±0.24)	0.48
1.0–2.5	0.94 (±0.22)	0.46

[a] p-Value of paired t-test of significance.
*Indicates ratios that are significantly different than 1.

and 0.32–1.0 μm indicate that these concentrations are not significantly different ($p = 0.46$ and $p = 0.48$, respectively).

Statistically significant differences, however, were observed between the concentrations of SMPS and MOUDI for the 0.1–0.32 and <0.1 μm ranges ($p < 0.001$ for both ranges). It is of particular interest to note that the SMPS concentrations are on average 1.37 (±0.35) times higher than those of the MOUDI for the 0.1–0.32 μm range, whereas the SMPS concentrations are lower than those of the MOUDI for the ultrafine PM mode, 0.39 (±0.18). There are several reasons that might explain this discrepancy between the two sampling methods, which does not seem to affect the overall excellent agreement obtained for total $PM_{2.5}$ mass concentrations. Previous studies have shown that MOUDI (and other impactors) may have particle bounce problems for particles as small as 0.2 μm, which cause the larger particles to be collected in lower stages (Pak et al., 1992; Cohen and McCammon, 2001). This could account for the observation that MOUDI underestimates mass for particles between 0.1 to 0.32 μm while overestimates mass for particles <0.1 μm compared with the SMPS. Particle bounce depends on several randomly varying factors, such as RH of the ambient air as well as particle concentration, which would also create a lack of correlation between the MOUDI and SMPS data consistent with the results shown in Fig. 8. Another possible reason that the two measurement methods disagree significantly for particles <0.32 μm is due to the particle sizing principle employed by each technique. The MOUDI classifies particles based on their aerodynamic diameter, hence inertia. By comparison, the SMPS classifies particles according to their mobility diameter, which to a first approximation depends on the surface area of the particles (Hinds, 1992). Conversions of mobility to aerodynamic diameter are based on the formula below (Sioutas et al., 1999):

$$\sqrt{C_a d_a} = \sqrt{\frac{C_{me}\rho_p}{\chi\rho_0}} d_{me},$$

where d_a is the aerodynamic diameter, d_{me} is the mobility equivalent diameter, C_a is the slip correction factor for the aerodynamic diameter, C_{me} is the slip correction factor for the mobility equivalent diameter, χ is the dynamic shape factor, ρ_p is the density of the particle, and ρ_0 is the unit density ($1\,g\,cm^{-3}$). When conversion from number to mass is determined, the particles are typically assumed to be perfect spheres ($\chi = 1$, $\rho_p = 1.6\,g\,cm^{-3}$) given that no other information on the morphological properties of ambient particles was available. The validity of this assumption, however, may be questionable in urban areas such as Los Angeles, in which a major portion of PM is emitted directly by millions of vehicles daily. Previous studies found that a significant fraction of the ultrafine particles in Los Angeles are agglomerate structures rather than spherical (Friedlander, 2000; Kim et al., 2001). These particles are primarily generated from high temperature combustion sources such as motor vehicles. By their very nature, agglomerate structures have higher surface areas than spherical particles with the same equivalent diameter, and are generally less dense (Weber et al., 1995). Because of their low density, a substantial fraction of these particles would be classified by an inertial separator (such as the MOUDI), as ultrafines, whereas the SMPS would classify these irregular particles in larger size ranges because of their high surface area and, hence, mobility. Similar observations have been made in a recent study by McMurry et al. (2002) in which the effective density of diesel-particles was measured by relating the mobility-measured diameter of combustion particles to their aerodynamic diameter. This study demonstrated that as the mobility size increases, the effective density tends to decrease presumably because of the surface irregularities of the larger particles (Ehara, 1996; McMurry et al., 2002; Park et al., 2001). It should be noted, however, that the relative abundance of these fractal-like agglomerates are highly variable, depending on the sampling location(s) as well as the time of day in order to account for the effect of vehicular emissions. Given the small contribution of ultrafine particles to the overall $PM_{2.5}$ mass, the observed differences did not introduce a significant disparity between the concentrations measured by the MOUDI and SMPS–APS. SMPS–APS measured $PM_{2.5}$ concentration may deviate substantially from those measured gravimetrically in locations where ultrafine PM may account for a sizable fraction of the overall fine particle mass.

4. Summary and conclusions

Size selective particle mass was measured on a semi-continuous basis by using an SMPS and APS. The SMPS–APS system was collocated with, and compared to, the Partisol filter and MOUDI Impactor samplers.

At the full range of $PM_{2.5}$ measurements, the SMPS–APS consistently compares well to gravimetrically determined reference mass concentrations of the Partisol and those of the MOUDI Impactor—both at separate locations and across different seasons for various time-intervals. However, the association between the SMPS–APS and Partisol is weakened for PM_{10}, which is driven by the poor efficiency of the APS for measuring coarse particle mass. This study corroborates the results of previous studies in that the APS: (1) overestimates coarse PM greater than about 4–5.5 μm, likely due to coincidence counting or the "phantom" effect; and (2) underestimates particles larger than about 6 μm due to a continuous increase of settling losses for larger particles in the sampling train of the APS.

Comparisons of the SMPS–APS demonstrate good agreement for particles larger than 0.3 μm. The differences between SMPS and MOUDI for smaller particles may be due to the effect of shape and density of local vehicular emissions on the measurement of particle mobility by the SMPS, resulting in its underestimation of ultrafine PM mass relative to the MOUDI. Additionally, particle bounce may occur at the lower stages of the MOUDI, and thus explain the MOUDI mass concentration being lower than the SMPS in the accumulation mode but higher in the UF mode.

Limited comparisons with the DataRAM, a continuous light scattering instrument, demonstrate a high correlation with the SMPS–APS. The DataRAM, however, measures about two-fold greater, on the average, and its response is especially greater between 0.7 and 1.0 μm, probably as a result of the Mie scattering.

While the coarse particle concentration measured by the APS may be biased due to sampling errors, our experiments showed that as a continuous $PM_{2.5}$ size selective mass monitor, the SMPS–APS is reliable and also offers several advantages over other continuous and time-integrated monitors. Notably, it is not subject to the potentially wide range of sampling, handling, and analysis errors to which filter-based mass measurements of PM are prone. Also, other semi-continuous mass monitors do not have the ability to simultaneously measure particle mass at selected sizes. Thus, the SMPS–APS system may be useful and convenient for source apportionment and health-based studies.

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